DIELECTRIC AND MICROSTRUCTURE BEHAVIOR OF LSMO: COBALT FERRITE NANOCOMPOSITE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
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By

Biswajit sahu
Roll No- 108CR0208

Department of Ceramic Engineering
National Institute of Technology
Rourkela

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National Institute of Technology
Rourkela

CERTIFICATE

This is to certify that the thesis entitled, "Dielectric and microstructure behavior of LSMO: cobalt ferrite nanocomposite", submitted by Mr. BISWAJIT SAHU (Roll no. 108CR0208) in partial fulfilment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any Other university / institute for the award of any Degree or Diploma.

B B Nayak
13/5/13

Prof. Bibhuti B. Nayak
Associate Professor
Department of Ceramic Engineering
National Institute of Technology
Rourkela- 769 008

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Biswajit Sahu.
13/5/13

BISWAJIT SAHU

109CR0208

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ABSTRACT

Manganite-ferrite nano composites are of interest due to its unusual magnetic and electrical properties. On the basis of technological importance, this nanocomposite can be used as magnetic tapes, sensing devices, read heads for hard disc & magnetic storage. In this work Microwave assisted synthesis was carried out for the preparation of (1-x) mol % $La_{0.67}Sr_{0.33}MnO_3$ (LSMO): x mol % $CoFe_2O_4$ (CF) (where x= 0, 30, 50, 70 and 100) nanocomposites using kitchen microwave oven. The Dielectric properties such as relative permittivity, loss factor, impedance value of these composites were measured. By varying with sintering temperature and frequency, the change in dielectric properties and microstructural behaviour were observed. The relative permittivity values and loss factor were found to be decrease with increase in frequency. The loss factor value was found to be negative in case of 70LSMO:30CF nanocomposite. The impedance value was also found to be decrease with increase in frequency. But in case of 70LSMO:30CF, where the LSMO percentage is higher, it increases first and then it decreases.

Key words- Manganite; Ferrite; Nano composites; Microwave synthesis; Microstructural; Dielectric properties

CHAPTER 1

INTRODUCTION

1.1 Structure and properties of manganites

The manganites show perovskite structure having the general formula $RE_{1-x}A_xMnO_3$ (RE = trivalent rare earth element such as Pr, La etc. and A = divalent alkaline earth ions such as Ca, Sr, Ba etc.). In perovskite structure, (RE, A) element are at the corner of a cube i.e. A-site and Mn occupies body centre of a cube i.e. B-site. Oxygen is at the face centres of the cube.[1,2] Manganites like $La_{1-x}Ca_xMnO_3$ (LCMO), and $La_{1-x}Sr_xMnO_3$ (LSMO), are of interest in recent past years as they show simultaneous electrical and magnetic transitions in certain composition ranges.[3] The perovskite manganites show the colossal magneto resistance (CMR) properties due to double ion exchange mechanism.[4]

The compound $La_{1-x}Sr_xMnO_3$ (LSMO) shows clear insulating behaviour at x=0, but Sr substitution for La leads to reduction of resistivity and for $0<x<0.7$ LSMO remain as insulating or semiconducting material.

$La_{0.67}Sr_{0.33}MnO_3$ (LSMO) shows different properties as compared to $La_{0.67}Ca_{0.33}MnO_3$ (LCMO). In LSMO, the A-site ion size is larger. The ferromagnetic metallic regime in case of LSMO extends over larger values of x as compared to LCMO. At room temperature LSMO has cubic perovskite structure but it changes to tetragonal structure above T_c. [5]

1.2 Structure and properties of ferrites

Ferrites (spinel structure) are generally ferrimagnetic compounds. The spinel have the general formula AB_2O_4, where A = divalent ions such as Fe^{2+}, Ni^{2+}, Co^{2+}, Mg^{2+}, Zn^{2+} and B=trivalent ions such as Al^{3+} and Fe^{3+} . In the spinel crystal structure the oxygen ions form a cubic close-packed and cations are filled in the octahedral (O) and tetrahedral (T) sites. The cubic unit cell comprises of 8 formula units having 32 Octahedral and 64 tetrahedral sites designated A and B sites respectively. Out of them 8 of the A sites and 16 of the B sites are occupied. There are two types of spinel such as normal and inverse spinel. In case of normal spinel, the divalent cations “A” are located in the tetrahedral (T) sites and the trivalent cations “B” are in the octahedral (O) sites. For example $ZnFe_2O_4$ has normal spinel structure. In the case of inverse spinel A site cation occupies half of the octahedral coordination and half the B site cation occupies the other half Octahedral sites as well as all tetrahedral sites. For example $CoFe_2O_3$ & $NiFe_2O_3$ have inverse spinel type structure.[6,17]

CF is known as hard magnetic material having high corecivity and moderate magnetization. It has a spinel or inverse spinel structure.[14] Due to these properties, CF is used for those applications such as high density magnetic storage materials, magnetic recording applications such as audio and video tapes, Ferro fluids and medical diagnosis.[2,9]

1.3 manganite: ferrite Nano composites

Nanocomposites of manganite and ferrite an insulating magnetic oxide are of interest because of their unusual magnetic as well as electrical properties.[14,17] In the case of composites made using La–Sr manganite and hard magnetic insulators such as Co-ferrite, it was found that magnetic coupling between the two phases affects the CMR behaviour. Thus this leads to an enhancement of electrical and magnetic properties of this nano composite. Nanocomposites are of interest because about 40 to 80 % of the atoms are in the grain boundaries and which leads to different properties as compared to the bulk material. Due to both fundamental and significant technological importance, the research on manganite-ferrite nano composites has been shown a great importance in recent years.[9,10]

CHAPTER 2

LITERATURE SURVEY

Many works have done to understand the electrical and magnetic properties of the manganite-ferrite based nanocomposite materials. There are different methods used to modify the electrical and magnetic properties like doping, grain size reduction, distribution of the manganite grains in a non-magnetic insulating matrix and magnetic insulating matrix.

Chun-Hua Yan et al. [14] have studied $La_{0.7}Sr_{0.3}MnO_3$ and $CoFe_2O_4$ samples which is prepared by a sol-gel process. The resistivity of the composite with 20 wt% $CoFe_2O_4$ is about an order of magnitude larger than that of the same-grain-sized $La_{0.7}Sr_{0.3}MnO_3$ sample, while a large low field magneto resistance (MR) has been found in case of composite. From the SEM image it was found that the large $CoFe_2O_4$ grain is continuously well surrounded by the nano LSMO grains. A large LFMR has been obtained in this composite compared to pure LSMO.

Yong Jun Seo et al. [13] have investigated the (1-x)LSMO/xZFO (x = 0, 0.01, 0.03, 0.06 and 0.09) composites which were prepared by a conventional solid-state method. From the XRD and SEM results it is found that LSMO and ZFO coexist in the composites and the ZFO mostly segregates at the grain boundaries region of LSMO. The resistivity of the samples was found to be increased by increasing the ZFO percentage. The metal-to-insulator (M-I) transition temperature of LSMO was decreased from 360K to 160K due to introduction of ZFO.

C.S. Xiong et al. [10] have studied the composites with compositions $La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ (LCSMO)/$x$$CoFe_2O_4$ (CFO) which was prepared by a standard ceramic technique. It was discussed that the influence of CFO phase on electrical properties and MR effect of the composites. From XRD and SEM it was found that there is no reaction between LCSMO and CFO in the composite. The change from one peak to two peaks in resistivity versus temperature curves may be caused due to both grain and grain boundary resistivity. This may be due to tunnelling of electrons and intrinsic transport properties of the samples.

Pawan Kumar et al. [6] prepared lanthanum doped cobalt ferrite ferrites synthesized by co-precipitation technique. The dielectric properties and magnetic properties of $CoLa_xFe_{2-x}O_4$ (x = 0, 0.1, 0.15, 0.2) ferrites have been investigated as a function of frequency and applied field. The values of dielectric constant and dielectric loss have been reduced due to incorporating of La^{3+} ions in cobalt ferrite. At room temperature the dc electrical resistivity of doped cobalt ferrite was found to increase up to 30 times as compared to pure cobalt ferrite.

Tian et al. [19] have studied $La_{0.67}Ca_{0.33}MnO_3/CuFe_2O_4$ composite which was prepared by sol-gel method. Microstructural, electrical and magnetic properties of these composites have been studied. The XRD and SEM analysis show that both $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) and $CuFe_2O_4$ phases are distributed in the composites. Compared with pure LCMO, an increase in magnetoresistance is observed over a wide temperature range for the composites due to intergrain tunnelling effect and magnetic coupling near boundaries between LCMO and $CuFe_2O_4$ grains.

Objective

In this present work, microwave assisted synthesis was carried out for the preparation of (1-x) mol % $La_{0.67}Sr_{0.33}MnO_3$ (LSMO): x mol % $CoFe_2O_4$ (CF) (where x= 0, 30, 50, 70 and 100) nanocomposites using kitchen microwave oven. Different characterizations techniques such as XRD, SEM, density measurement and dielectric test have been performed and the results have been discussed in detail.

CHAPTER 3

EXPERIMENTAL ANALYSIS

3.1. Microwave synthesis of LSMO & CF as well as LSMO: CF Composite

For preparation of pure LSMO powder, stoichiometric equivalents of La-acetate, Sr-chloride, Mn-acetate and for preparation of pure CF powder, stoichiometric equivalents of cobalt chloride and Iron chloride were taken and that mixtures were mixed with ethylene glycol. For the composite preparation (1-x) mol % $La_{0.67}Sr_{0.33}MnO3$ (LSMO): x mol % CoFe2O4 (CF) (where x= 0, 30, 50, 70 and 100) were taken and glycol was added to each case. The individual solution was heated at 80 °C under constant magnetic stirring condition. These solutions were found to be acidic so KOH solution was added to the precursor solution to increase the pH value. The initial solution becomes a clear solution and form a gel at pH = 12.5. These gel precursors were taken for microwave refluxing. Generally 2.5 GHz frequency and 980 Watts was used to heat the precursor solution to the temperature 473 K which is the boiling point of ethylene glycol. After that this solution was condensed by refluxing with circulated water and recycled. Refluxing was done for 1hr with 5min interval. Now the precipitate obtained was washed thoroughly with distilled water to get pH 7 and dried. The dried powers were calcined at 800^0C and then pelletized using 4Ton pressure for 90 sec. 1-2 wt. % poly vinyl alcohol (PVA) was used as binder, and then the pellets were sintered at two different temperatures i.e. at 1200^0C and 1300^0C. Structure, microstructure and dielectric properties of these sintered samples have been studied and analysed.

3.2 General characterization

3.2.1. Density

Density was measured by Archimedes principle where the pellets were kept in kerosene medium inside a vacuum chamber for 1hr. The dry weight, soaked weight and suspended weight, were taken to calculate bulk density using the following formula.

Bulk Density= D/ (W-S) * density of liquid medium

Where D= Dry wt. of the sample, W=Soked wt. of sample & S=Suspended wt. of sample

Liquid medium in this case is kerosene with density of 0.80 g/cc. The density of different composition was measured i.e. for 30LSMO:70CF, 50LSMO:50CF and 70LSMO:30CF which were annealed at 1200 °C, 1300 °C. Similarly the apparent porosity of the sintered pallets was determined which will give an idea regarding the overall density of the LSMO-CF composite material. Similarly apparent porosity was measured by the following formula.

Apparent porosity (AP) = W-D/ (W-S) *100

Where W, D, S stands for similar meaning as that of the above.

3.2.2. Scanning Electron Microscope

Microstructural features were studied using Scanning Electron Microscope (JSM 6480 LV JEOL, Japan). For preparation of SEM sample, the pellets were placed in acetone in an ultra-sonication bath (20 kHz, 500 W) for half an hour. After sonication platinum coating was done by sputtering for conducting purpose. The images were taken in back scattered electron (BSE) mode to distinguish the two phases present in the composites and the grain size of different phases were analysed.

3.2.3. Dielectric properties Measurement

The dielectric properties such as relative permittivity, loss factor, impedance, and resistivity were measured using solartron (dielectric interface) and impedance analyzer at room temperature with increasing in frequency. The frequency varies from 1Hz to 1 MHz. The dielectric properties were measured for different samples, which were sintered at 1200^0C and 1300^0C.

CHAPTER 4

RESULTS & DISCUSSION

4.1.1 Density

The density of pure LSMO and pure CF are given in Table 4.1 and 4.2, respectively. The density was at an average more than 85% was observed for these pure LSMO and CF.

Table 4.1 Density of pellets of pure LSMO and Pure CF sintered at 1200^0C

	Samples	Dry Weight (g)	Suspended Weight(g)	Soked Weight (g)	Bulk density (g/cc)	Relative density (in %)
Pure LSMO	Sample 1	0.605	0.530	0.618	5.5	85.66
	Sample 2	0.615	0.542	0.636	5.59	87.07
Pure CF	Sample 1	0.628	0.548	0.657	4.6	89.49
	Sample 2	0.612	0.539	0.645	4.61	89.68

Table 4.2 Density of pellets of pure LSMO and Pure CF sintered at 1300^0C

	Samples	Dry Weight (g)	Suspended Weight(g)	Soked Weight (g)	Bulk density (g/cc)	Relative density (in %)
Pure LSMO	Sample 1	0.6075	0.535	0.621	5.67	88.31
	Sample 2	0.627	0.552	0.639	5.76	89.71
Pure CF	Sample 1	0.635	0.565	0.673	4.7	91.26
	Sample 2	0.618	0.536	0.639	4.79	92.41

The density of 70LSMO:30CF, 50LSMO:50CF and 30LSMO:70CF are given in Table 4.3 (sintered at 1200^0C) and Table 4.4. (sintered at 1300^0C). An average of nearly 90% density was found for different types of composites.

Table 4.3 Density of pellets of LSMO: CF composites sintered at 1200^0C.

LSMO:CF (mol %)	Dry Weight (g)	Suspended Weight(g)	Soked Weight (g)	density (In %)
70:30	0.789	0.718	0.790	87.6
50:50	0.704	0.649	0.594	89.93
30:70	0.645	0.594	0.651	90.52

Table 4.4 Density of pellets of LSMO: CF composites sintered at 1300^0C.

LSMO:CF (mol %)	Dry Weight (g)	Suspended Weight(g)	Soked Weight (g)	density (In %)
70:30	0.703	0.633	0.695	90
50:50	0.686	0.632	0.694	91.46
30:70	0.674	0.624	0.682	92.96

The density of LSMO: CF composite plays a very important role in the enhancement of dielectric properties. It is found that density increases with increase in CF content and highest density was obtained for 70 mol % CF additions. Also found that density of sample sintered at 1300°C is higher than the samples sintered at 1200°C. More than 90% density was observed for all composites.

4.1.2Microstructure

SEM micrographs of pure sintered LSMO and CF samples are shown in Fig. 4.1 (a) and (b), respectively. SEM micrographs of sintered LSMO: CF nanocomposite sample is shown in Fig. 4.2.

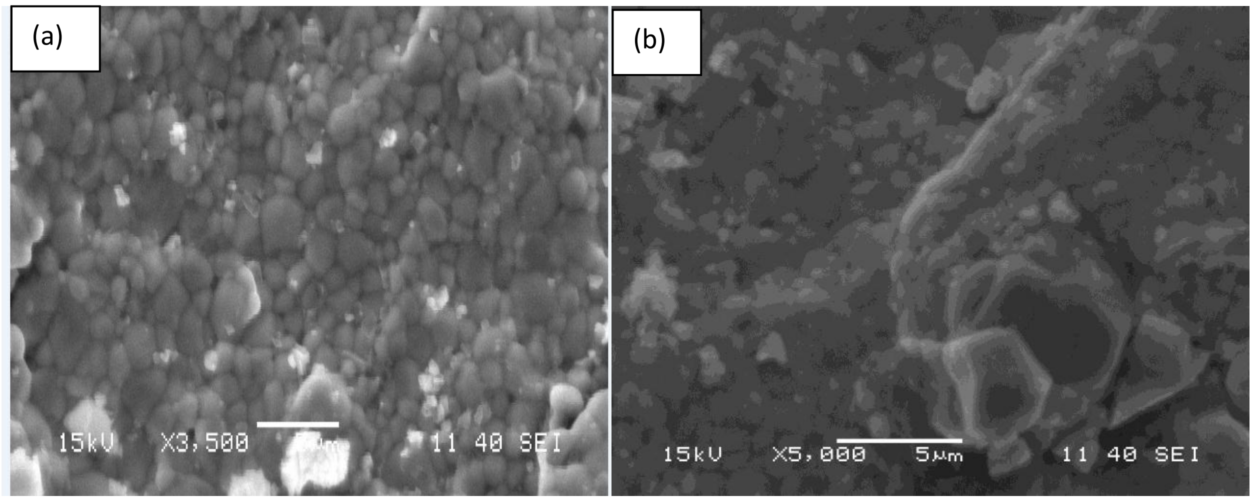


Fig. 4.1: SEM micrographs of pure sintered (a) LSMO (b) CF pellet

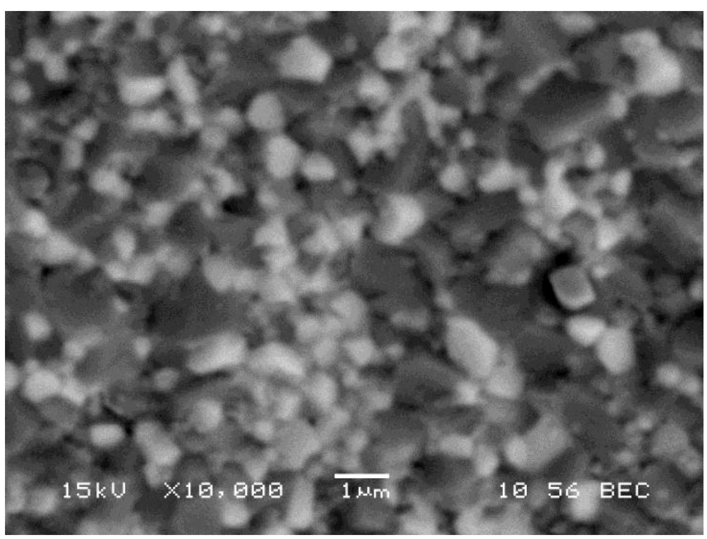


Fig. 4.2: SEM micrographs of sintered LSMO: CF composite

The particle size of pure CF is comparatively large as compared to pure LSMO, as seen from the SEM micrographs. The grain size of pure CF shows irregular in shape. However, the grain size of LSMO was nearly spherical in nature. The density is strongly related to the above microstructure and it was found that LSMO was comparatively more density than CF due to small grain size as well as distribution of grains.

It was confirmed from the SEM image that the LSMO and CF phases were well distributed with uniform size of around 1 μm. In SEM micrograph (Fig. 4.3), the white portions indicate the presence of LSMO phase and the black portion indicates the presence of CF phase. The density of this composite was found to be more than 90 % of the theoretical density.

4.1.3 Dielectric properties

Relative permittivity

Permittivity (ε) is a measure of the ability of a material to be polarized by an electric field. By applying different frequency we examine the relative permittivity value with respect to frequency and the results have been shown in Fig. 4.3 (relative permittivity vs. frequency for 30LSMO:70CF, 50LSMO:50CF, 70LSMO:30 CF).

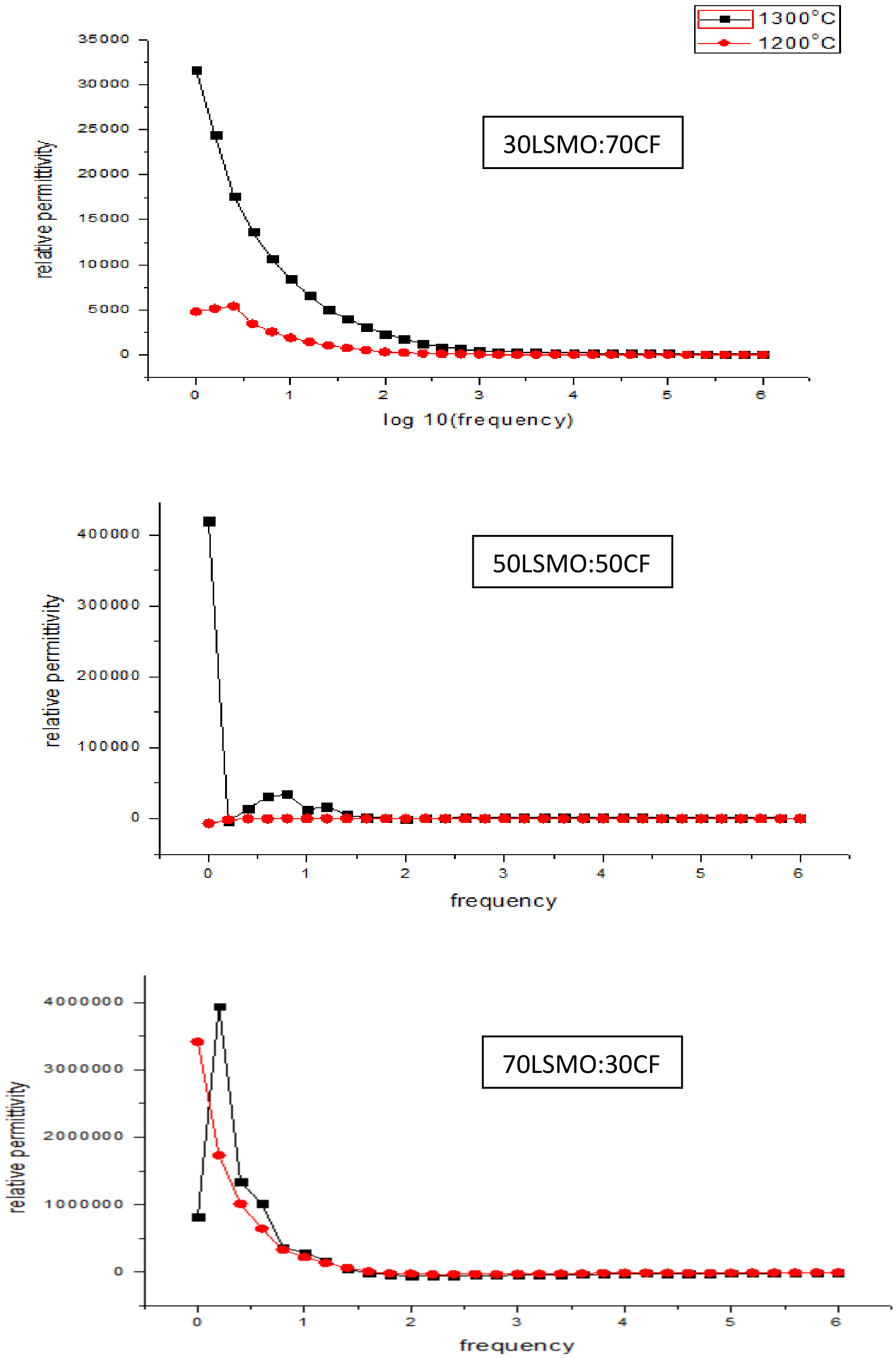


Fig. 4.3: relative permittivity vs. frequency curve of different LSMO: CF composites

The relative permittivity value decreases with increase in frequency. At low frequency, charges are accumulated at the border region causes the interfacial polarization i.e. space charge polarization, so the value is high. But at higher frequency the value decreases and remains constant due to inability of electric dipoles to the fast variation alternating applied field. The relative permittivity value of the sample sintered at 1300^0C is higher than sintered at 1200^0C due to higher densification of sample at 1300^0C. Overally the relative permittivity value of 30LSMO:70CF was higher as compared to other composites due to higher CF content. The CF act as an insulating phase in the composite which helps in increasing the permittivity value.

Again from the permittivity value, the dielectric constant of this composite can be calculated by using the following relationship.

The dielectric constant $k = \varepsilon/\varepsilon o$.

The dielectric constant is therefore also known as the relative permittivity of the material. Since the dielectric constant is just a ratio of two similar quantities, it is dimensionless. So in this case as the relative permittivity value decreases with increase in frequency, so dielectric constant also decreases with increase in frequency. The dielectric constant value is higher in 30LSMO:70CF phase.

Loss factor (tan delta)

The tangent of dielectric loss angle can be calculated using the relation equation

$$\tan\delta = \frac{1}{2\pi f R_s C_s},$$

Where δ is the loss angle, f is the frequency, R_s is the equivalent series resistance and C_s is the equivalent series capacitance. The dielectric loss factor (ε') is also measured in terms of tangent loss factor ($\tan\delta$) defined by the relation, $\varepsilon'' = \varepsilon' \tan\delta$.

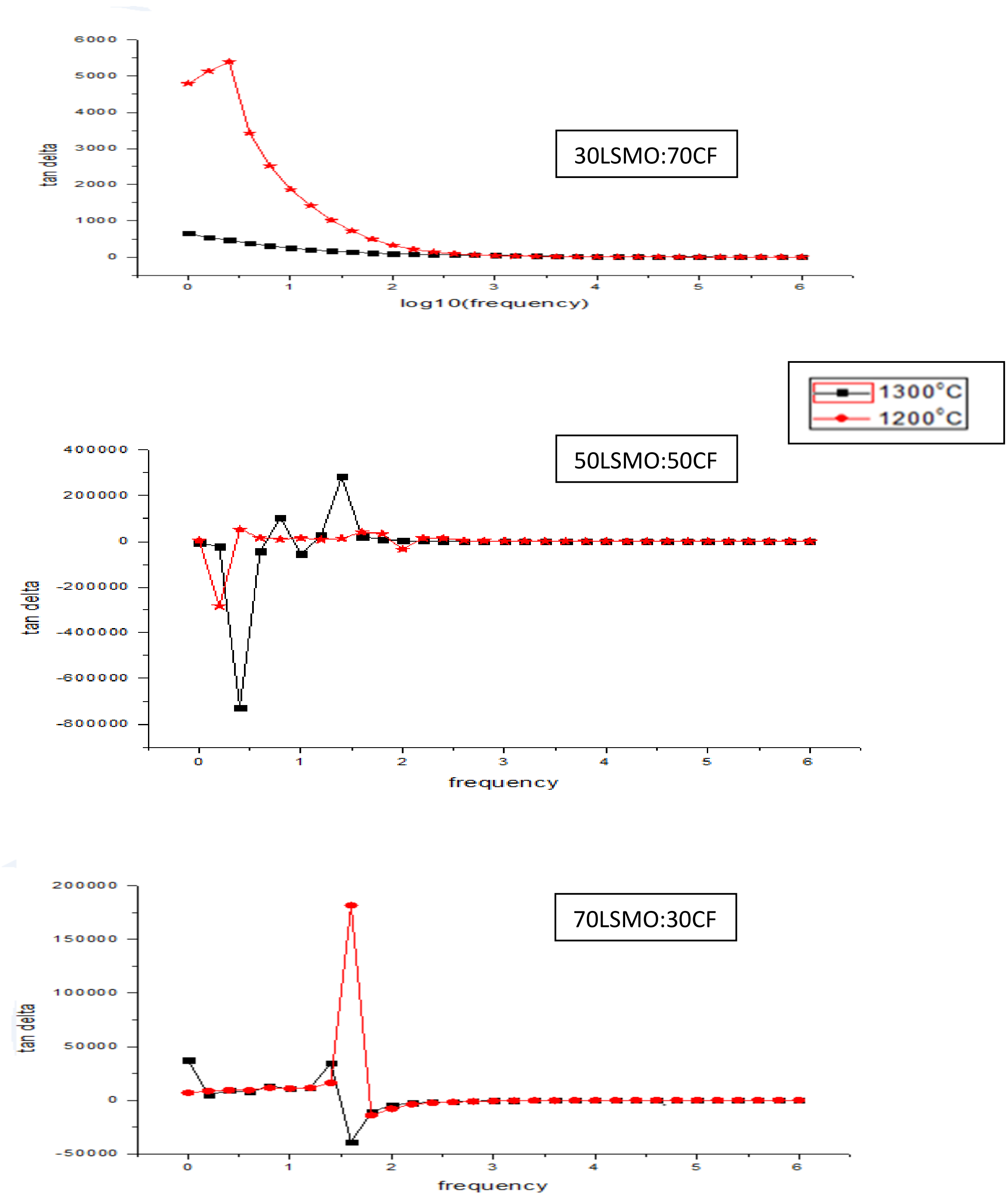
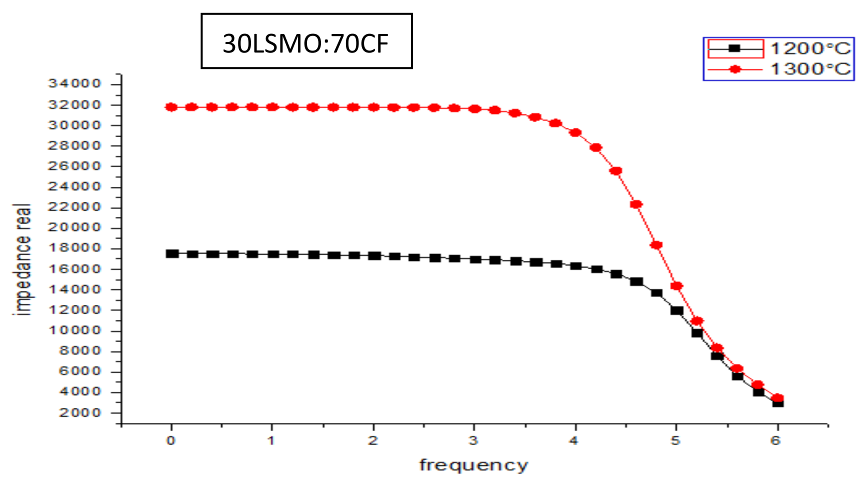


Fig. 4.4: Loss factor vs. frequency of different LSMO: CF composites

From the above Fig. 4.4, it has been examine that the loss factor (tan delta) value first decreases and remains constant in most cases with increase in frequency. At higher frequency due to hopping mechanism the resistivity value decreases sharply means it's become conducting. Dielectric loss is especially high around the relaxation or resonance frequencies of the polarisation mechanisms as the polarisation lags behind the applied field, causing an interaction between the field and the dielectric's polarisation that results in heating. The tan delta value is found to be negative in case of 50LSMO:50CF & 70LSMO:30CF due to low percentage of CF.

Impedance

The impedance vs. frequency curves of different LSMO: CF composites are shown Fig.4.5.



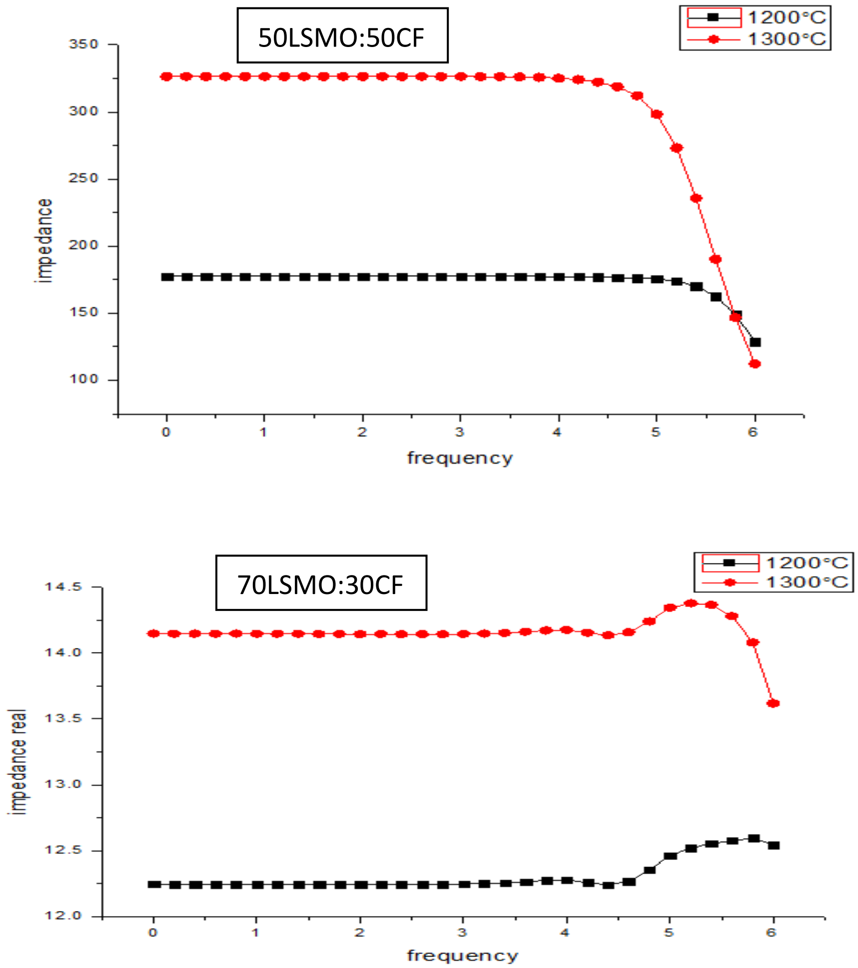


Fig. 4.5: impedance real vs. frequency of different LSMO: CF composites

From the Fig 4.5, it has been found that the impedance real value remain constant up to certain value and after that decreases at higher frequency. The impedance value decrease due to the skin effect, as higher frequency skin depth is lower causes the effective resistance of conductor. This impedance real value increases with increase in CF percentage, so 30LSMO:70CF has the value.

Similarly, impedance (imaginary) vs frequency of different LSMO: CF composites are shown in Fig. 4.6.

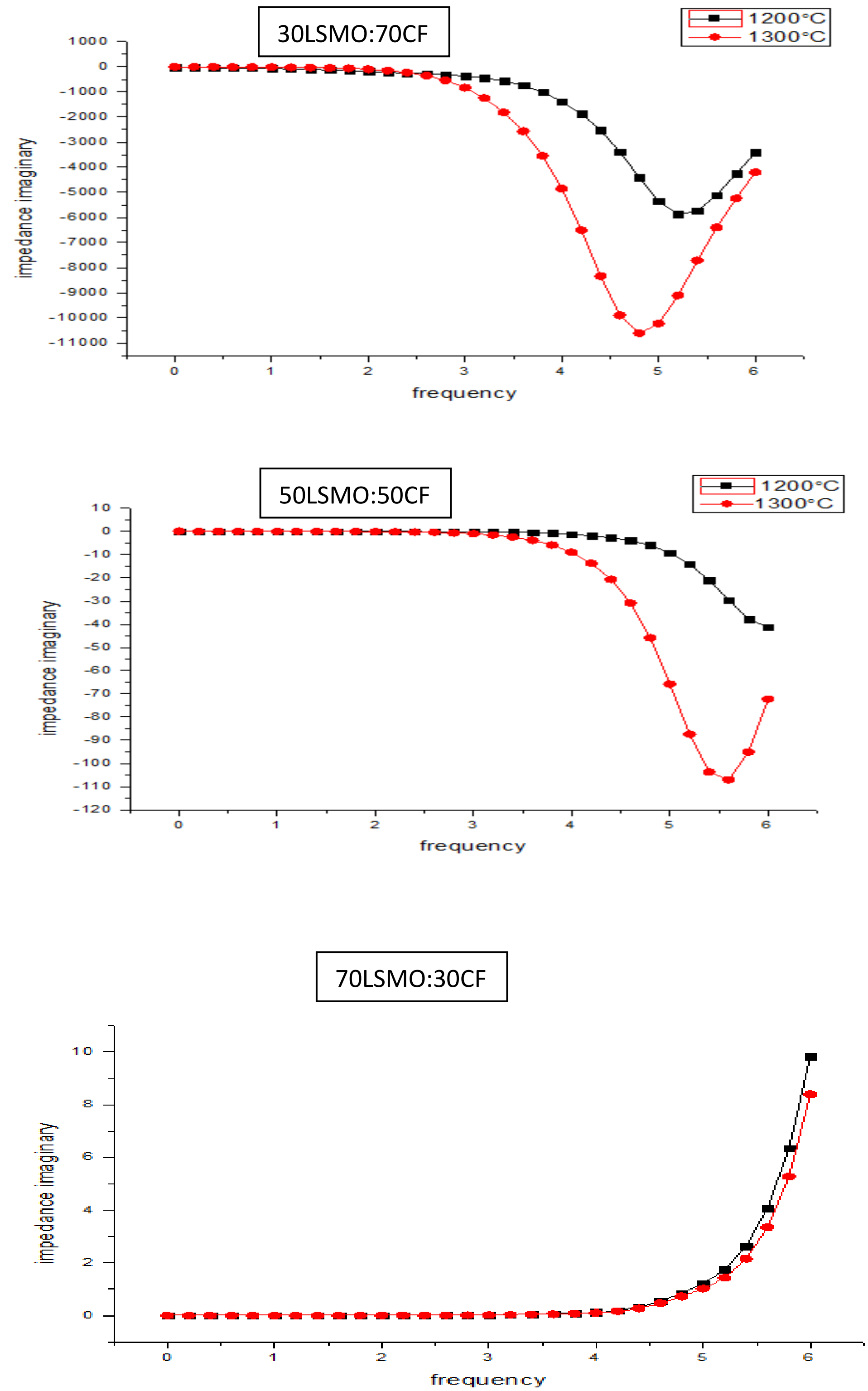


Fig. 4.6: impedance imaginary vs. frequency for 30LSMO:70CF, 50LSMO:50CF, 70LSMO:30CF

In the above graphs (Fig. 4.6), the impedance imaginary value decreases with increase in frequency, then decreases in first two cases i.e. in case of 30LSMO:70CF & 50LSMO:50CF .But incase of 70LSMO:30CF, the value increases with increase in frequency. At higher frequency, the value decreases due to skin effect .The impedance value increases with increase cobalt ferrite percentage. The impedance value also decreases with increase in frequency due the hopping mechanism.

4.2.5 Summary

Nanocomposites of LSMO and CF were successfully prepared by using microwave refluxing synthesis route. The microstructural and dielectric properties of LSMO: CF composites are different from each other. The two phase system is clearly seen from SEM image. The grain size of all composites shows irregular shape. Maximum permittivity value was found in case of 30LSMO:70CF due more percentage of CF, which is an insulating oxide. The loss factor value also showing negative due to presence of more LSMO phase i.e in 50LSMO:50CF & 70LSMO:30CF composites.

5.1 Conclusions

The findings of this present work are summarized as follows:

1. It is possible for successful preparation of LSMO: CF composite material by microwave refluxing technique. This synthesis method plays a vital role for making a dense sample having well defined microstructure.
2. From the SEM image it has been found that the grain sizes of LSMO is smaller than that of CF grain and the grains are found to be spherical and irregular in nature.
3. The relative permittivity value decreases with increasing frequency. This is due to the space charge polarization.
4. The relative permittivity value increases with increase in sintering temperature.
5. The loss factor (tan delta) value decrease with increase in sintering temperature as the density percentage increases with increase in temperature.
6. The impedance value was also increases with increase in CF content i.e. for 30LSMO:70CF the impedance value is higher.

5.2 Future work

The present work leaves a wide scope for future investigators to explore many other aspects like its electrical effect, magneto-electric effect at low frequency and high frequency, colossal magneto resistance (CMR) applications. The effect of magnetic properties with dielectric property can be studied for low frequency as well as high frequency application.

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